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**Methyl Tin(IV) Derivatives of HOTeF_5 and $\text{HN}(\text{SO}_2\text{CF}_3)_2$: A
Solution Multi-NMR Study and X-ray Crystal Structures of
 $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ and $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$**

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This paper is dedicated to our dear friend and colleague Karl O. Christe for his outstanding achievements in the field of Inorganic Chemistry

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Abstract

The new tin(IV) species, $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$, was prepared via solvolysis of $(\text{CH}_3)_3\text{SnCl}$ in HOTeF_5 or from the reaction of $(\text{CH}_3)_3\text{SnCl}$ with ClOTeF_5 and was characterized by NMR and vibrational spectroscopy, mass spectrometry, and single crystal X-ray diffraction. $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ crystallizes in the monoclinic space group $P2_1/n$ ($a = 5.8204(8) \text{ \AA}$, $b = 10.782(1) \text{ \AA}$, $c = 15.493(2) \text{ \AA}$, $\beta = 91.958(2)^\circ$, $V = 971.7(2) \text{ \AA}^3$, $Z = 4$). NMR spectroscopy of $(\text{CH}_3)_3\text{SnX}$, prepared from excess $\text{Sn}(\text{CH}_3)_4$ and HX ($\text{X} = \text{OTeF}_5$ or $\text{N}(\text{SO}_2\text{CF}_3)_2$), revealed a tetracoordinate tin environment using $(\text{CH}_3)_3\text{SnX}$ as a neat liquids or in CH_2Cl_2 solutions. In acetone and CH_3CN solution, the tin atom in $(\text{CH}_3)_3\text{SnOTeF}_5$ was found to extend its coordination number to five by adding one solvent molecule. In the strong donor solvent, DMSO, the Sn-OTeF_5 bond is broken and the $(\text{CH}_3)_3\text{Sn}(\text{O}=\text{S}(\text{CH}_3)_2)_2^+$ cation and the OTeF_5^- anion are formed. $(\text{CH}_3)_3\text{SnOTeF}_5$ and $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ show different reactivity with water. While the OTeF_5 group of $(\text{CH}_3)_3\text{SnOTeF}_5$ undergoes complete hydrolysis, $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ forms the stable hydrate salt, $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$. This salt crystallizes in the monoclinic space group $P2_1/c$ ($a = 7.3072(1) \text{ \AA}$, $b = 13.4649(2) \text{ \AA}$, $c = 16.821(2) \text{ \AA}$, $\beta = 98.705(1)^\circ$, $V = 1636.00(3) \text{ \AA}^3$, $Z = 4$) and was also characterized by NMR and vibrational spectroscopy.

Introduction

The solvolytic reactions of alkyltin(IV)chlorides in strong protonic acids, such as HF,¹ HOSO₂F, HOSO₂CF₃, and HOPOF₂,²⁻⁴ and the superacidic HF-MF₅ (M = Sb, Nb, Ta) systems,⁵ are a convenient preparative route to the corresponding organotin(IV) derivatives. In these acidolysis reactions, Sn-Cl as well as Sn-C bond cleavage have been observed, with Sn-Cl bond cleavage being preferred. Alkyl tin(IV) derivatives of acids are commonly polymeric due to vacant coordination sites on tetracoordinate tin(IV). The bridging occurs through halogen atoms or the oxoacid ligands. In the solid state, the methyl tin halides, (CH₃)₃SnF^{6,7} and (CH₃)₃SnCl⁸, form extended halogen-bridged chains with pentacoordinate tin, while (CH₃)₂SnF₂⁹ has a sheet-like polymeric structure with hexacoordinate tin. The crystal structures of (CH₃)₂Sn(SO₃F)₂,¹⁰ (CH₃)₃SnOOCCF₃,¹¹ (C₆H₁₂)₃SnOOCCH₃,¹² and (CH₃)₂SnCl(OOCCH₃)¹³ contain tin centers that are bridged by the oxoacid ligands. However, due to steric crowding tricyclohexyltin(IV) trifluoroacetate contains only a four-coordinated tin.¹⁴ While chlorodimethyltin(IV) species, such as (CH₃)₂SnCl(OOCCH₃), contain a five-coordinated tin with bridging acetate groups,¹³ the corresponding diethyl species exhibits a distorted trigonal bipyramidal structure involving chlorine-bridges.¹⁵

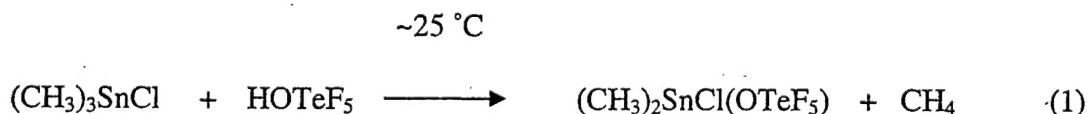
Alternative synthetic routes to such alkyltin(IV) derivatives involve metathetical reactions of alkyltin(IV) chlorides with Ag⁺ salts of the corresponding acids,^{5,16-19} and reactions with chloro derivatives of the acids.¹⁸ Alkyltin(IV) derivatives of the nitrogen acids, HN(SO₂X)₂ (X = F, CF₃), have been prepared by the metathetical reaction of (CH₃)₃SnCl with [Ag][N(SO₂X)₂]·C₆H₆¹⁷ and by the reaction of (CH₃)₃SnCl with ClN(SO₂X)₂.¹⁸ Solutions of (CH₃)₃SnN(SO₂X)₂ (R = alkyl; X = F, CF₃) have been studied by multi-NMR spectroscopy in various solvents, showing that these species contain highly electron deficient tin centers.^{17,18}

The extreme case of electron deficient tin center is exemplified by tricoordinate stannyl cations. Recently, the Mes_3Sn^+ cation (mes = mesityl) has been prepared in solution by Lambert et al. and characterized by its highly deshielded ^{119}Sn resonance at 806 ppm.²⁰ The closest approximation to a stannyl cation in the solid state to date is the $[\text{n-Bu}_3\text{Sn}][\text{CB}_{11}(\text{CH}_3)_{12}]$ salt that has been characterized by X-ray crystallography.²¹

To our knowledge, $(\text{CH}_3)_3\text{SnOTeF}_5$ is the only known tin compound that contains an OTeF_5 group, but no detailed structural characterization has been carried out.¹⁹ The acid strength of HOTeF_5 , which was found to lie between those of HNO_3 and HCl ,²² is larger than those determined for the nitrogen acids $\text{HN}(\text{SO}_2\text{X})_2$, i.e., $\text{pK}_a = 1.3$ ($\text{X} = \text{F}$),²³ $\text{pK}_a = 1.7$ ($\text{X} = \text{CF}_3$).²⁴ The exceptionally high group electronegativity of the OTeF_5^- group (3.87)²⁵ has been commented on by Schrobilgen et al.,²⁵ Seppelt,²⁶ and Christie²⁷ and lies slightly above those of $\text{N}(\text{SO}_2\text{X})_2$ groups (~ 3.6 on the Pauling scale for the latter).²³ This property of the OTeF_5 group, can be employed to synthesize highly electron deficient organotin(IV) species. The present study was undertaken to investigate the reactions of $(\text{CH}_3)_3\text{SnCl}$ with HOTeF_5 and ClOTeF_5 .

Results and Discussion

Syntheses and Properties of $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ and $(\text{CH}_3)_3\text{SnOTeF}_5$. The reaction of $(\text{CH}_3)_3\text{SnCl}$ with a slight excess of HOTeF_5 in the absence of a solvent yielded colorless $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ as the major Sn(IV) product according to eq. (1). The by-



product, methane, was identified by infrared spectroscopy. Solid $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ can be sublimed at 50°C (0.01 Torr). This result is in contrast to the previously reported preparation of

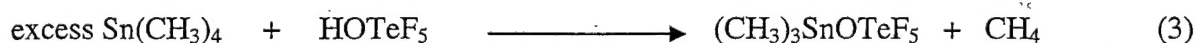
$(\text{CH}_3)_3\text{SnOTeF}_5$ via the solvolysis reaction of $(\text{CH}_3)_3\text{SnCl}$ in HOTeF_5 .¹⁹ Under our experimental conditions, only minor amounts of $(\text{CH}_3)_3\text{SnOTeF}_5$ were detected by ^{119}Sn NMR spectroscopy, and the major product was $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$. The formation of $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ indicates that either the Sn-C bond is cleaved preferentially compared to the Sn-Cl bond or that the Sn-Cl bond is initially cleaved forming $(\text{CH}_3)_3\text{SnOTeF}_5$ and HCl as intermediates, followed by attack of HCl , thereby forming $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ and CH_4 . The propensity of hydrogen halides to cleave as many as two Sn-C bonds has been well established.²⁸ The reaction of $(\text{CH}_3)_3\text{SnCl}$ with trifluoroacetic acid has also been reported to result in the replacement of a methyl group.²⁹

Surprisingly, $(\text{CH}_3)_3\text{SnCl}$ also reacts with ClOTeF_5 in CFCl_3 solvent to form $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ according to eq. (2) where methylchloride was identified as the reaction

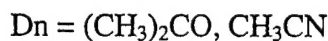
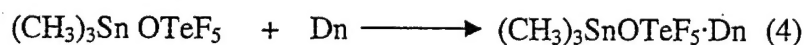


product. A minor component was also identified by ^{119}Sn NMR and is assigned to $[(\text{CH}_3)_2\text{SnO}(\text{OTeF}_5)]_n$ based upon preliminary x-ray diffraction analysis. Investigation of three separate crystals yielded twinned samples and so far, we have not been able to refine the structure satisfactorily. The formation of this product can be explained by the hydrolysis of one OTeF_5 groups in $(\text{CH}_3)_2\text{Sn}(\text{OTeF}_5)_2$ followed by polymerization via formation of Sn-O-Sn bonds.

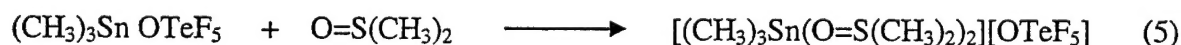
Pure $(\text{CH}_3)_3\text{SnOTeF}_5$ can easily be prepared in quantitative yield by the solvolysis of HOTeF_5 in a large excess of $\text{Sn}(\text{CH}_3)_4$ with the elimination of methane as previously reported¹⁹ (eq. (3)).



The clear, colorless, mobile liquid, $(\text{CH}_3)_3\text{SnOTeF}_5$, is far less viscous than the fluid-like $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{X})_2$ ($\text{X} = \text{F}$ or CF_3).^{17,18} In the presence of donor solvents such as $(\text{CH}_3)_2\text{CO}$ (donor number, $\text{DN} = 17.0$)³⁰ and CH_3CN ($\text{DN} = 14.1$),³⁰ $(\text{CH}_3)_3\text{SnOTeF}_5$ forms adducts in solution (eq. (4)) which were characterized by NMR spectroscopy (see NMR Spectroscopy (a)).

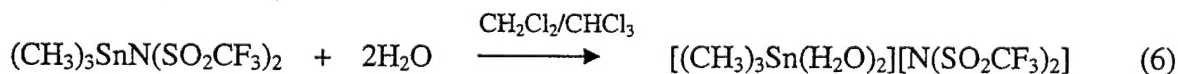


The even stronger donor solvent DMSO ($\text{DN} = 29.8$)³⁰ causes a solvent assisted dissociation of the Sn-O bond yielding the $(\text{CH}_3)_3\text{Sn}(\text{O}=\text{S}(\text{CH}_3)_2)_2^+$ cation and the OTeF_5^- anion in solution (eq. (5))



which were characterized by NMR spectroscopy. Unlike $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ which forms adducts with water (vide infra), $(\text{CH}_3)_3\text{SnOTeF}_5$ reacts with water in CH_3CN and DMSO solvents resulting in hydrolytic degradation of the OTeF_5 group as evidenced by the appearance of numerous signals in the ^{125}Te and ^{19}F NMR spectra.

Synthesis and Properties of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$. The reaction of $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ with water in a mixture of $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ resulted in dissociation of $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ and the formation of colorless crystals of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ according to eq. (6). Under the present conditions, no degradation of the $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ anion was observed.



Vibrational Spectroscopy. The vibrational spectra of $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$, $(\text{CH}_3)_3\text{SnOTeF}_5$, and $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ together with their tentative assignments are listed in the experimental section.

(a) $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ and $(\text{CH}_3)_3\text{SnOTeF}_5$. The frequencies of the Te-O stretching vibration in OTeF_5 derivatives lie in the range $868\text{--}613\text{ cm}^{-1}$.^{31,32} This variation in $\nu(\text{Te-O})$ band is attributed to the partial double bond character in the OTeF_5^- anion.³³ The $\nu(\text{Te-O})$ bands for $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ and $(\text{CH}_3)_3\text{SnOTeF}_5$ both lie at 860 cm^{-1} in the infrared and at 856 cm^{-1} in the Raman spectra indicating a similar bonding situation in both tin pentafluorotellurate species.

(b) $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$. The infrared spectrum of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2]\text{N}(\text{SO}_2\text{CF}_3)_2$ shows additional bands attributable to the coordinated water molecules, when compared to that of its parent compound, $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$.¹⁸ The infrared bands associated with the $\text{N}(\text{SO}_2\text{CF}_3)_2$ group are slightly shifted. The most significant shift is found for the antisymmetric SO_2 stretch of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ which appears at lower frequency (1346 cm^{-1}) relative to that of $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ (1378 cm^{-1}).¹⁸ The $\nu_{\text{as}}(\text{SO}_2)$ stretching band is diagnostic of sulfonamide groups and is lowered by about 100 cm^{-1} upon going from covalent to ionic derivatives as a consequence of the delocalization of the negative charge of sulfonamide anions onto the sulfonyl oxygen atoms, resulting in weaker S=O bonds.^{17,34} For ionic $\text{N}(\text{SO}_2\text{CF}_3)_2$ groups $\nu_{\text{as}}(\text{SO}_2)$ frequencies of 1345 cm^{-1} have been reported which is in excellent agreement with that observed for $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ corroborating its ionic nature that was observed by X-ray crystallography (see Crystal Structures (b)).

NMR Spectroscopy. The multi-NMR spectroscopic data of $(\text{CH}_3)_3\text{SnOTeF}_5$ as a neat liquid and in various solvents, and those of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ in CH_3CN , and

DMSO solvents are listed in Tables 1 and 2, together with the literature data for

$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ ¹⁸ and $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$.¹⁷

(a) $(\text{CH}_3)_3\text{SnOTeF}_5$. The ^{119}Sn chemical shift of $(\text{CH}_3)_3\text{SnOTeF}_5$ is highly dependent upon the nature of the solvent. The ^{119}Sn resonances for $(\text{CH}_3)_3\text{SnOTeF}_5$ in CH_2Cl_2 solvent (272.4 ppm) and as a neat liquid (270.8 ppm) are ca. 20 ppm more deshielded than that of the $\text{N}(\text{SO}_2\text{X})_2$ ($\text{X} = \text{F}, \text{CF}_3$) substituted trimethyl tin derivatives^{17,18} and are at significantly higher frequencies compared to the previously suggested range of 200 to -60 ppm for tetracoordinated organotin(IV) derivatives.^{35,36} This indicates a highly ionic Sn-O bond and a highly electron deficient tin center in $(\text{CH}_3)_3\text{SnOTeF}_5$. In donor solvents such as $(\text{CH}_3)_2\text{CO}$, CH_3CN , and DMSO, the ^{119}Sn resonance is shifted to significantly lower frequency as previously reported for dialkyl and trialkyl tin(IV) species.^{17,18,35,36} This increase in shielding is indicative for an increase in coordination number from four to five upon adduct formation with the donor solvent.

Lockhart^{37,38} suggested empirical correlations between the $^2J(^{119}\text{Sn}-^1\text{H})$ and $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants in methyltin compounds and the average C-Sn-C angles (eqs (7) and (8)).

$$\theta = 0.0161 |^2J(^{119}\text{Sn}-^1\text{H})^2| - 1.32|^2J(^{119}\text{Sn}-^1\text{H})| + 133.4 \quad (7)$$

$$|^1J(^{119}\text{Sn}-^{13}\text{C})| = 11.4\theta - 875 \quad (8)$$

The C-Sn-C angles calculated using both equations are listed in Table 1. The C-Sn-C angles calculated for the neat $(\text{CH}_3)_3\text{SnOTeF}_5$ or the CH_2Cl_2 solution are close to the tetrahedral angle of 109.5° . In donor solvents, the $^2J(^{119}\text{Sn}-^1\text{H})$ and $^1J(^{119}\text{Sn}-^{13}\text{C})$ are larger by approximately 10 Hz reflecting an increase in the s-electron density in orbitals at tin involved in bonding to the methyl groups. As a consequence, the calculated C-Sn-C angles are close to 120° which is

consistent with a trigonal bipyramidal geometry with the three methyl groups in the equatorial position.

The ^{19}F NMR spectra of OTeF_5 derivatives also provide information about the extent of bond polarization. An increase in electron density on the oxygen atom reaching a maximum for the OTeF_5^- anion increases the O-Te back bonding which in turn causes a weakening of the Te-F_{ax} bond and results in increased shielding of the axial fluorine resonance and a decrease in $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{ax}})$.³³ The NMR spectroscopic parameter for the OTeF_5 group in $(\text{CH}_3)_3\text{SnOTeF}_5$ dissolved in CH_2Cl_2 , $(\text{CH}_3)_2\text{CO}$, CH_3CN , and as a neat liquid are in the same range ($^{19}\text{F}_{\text{ax}}$: ca -30 ppm; $^{19}\text{F}_{\text{eq}}$: ca -40 ppm; ^{125}Te : 565 to 575 ppm; $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{ax}})$: 3020 to 3188 Hz; and $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{eq}})$: ca 3550 Hz) reflecting only slight changes to the electronic structure of the OTeF_5 ligand. The solution of $(\text{CH}_3)_3\text{SnOTeF}_5$ in DMSO, however, exhibits significantly different shifts and coupling constants. The $^{19}\text{F}_{\text{ax}}$ chemical shift and $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{ax}})$ coupling constant appear at higher frequency (-16.2 ppm) and are smaller, respectively, and are consistent with values found for $[\text{N}(n\text{-Bu})_4][\text{OTeF}_5]$.³³ This suggests the presence of an OTeF_5^- anion in solution as a consequence of the dissociation of $(\text{CH}_3)_3\text{SnOTeF}_5$ upon adduct formation with two strong donor molecules of DMSO (cf eq. (4)). The donor-solvent assisted ionization of a trialkyl tin(IV) derivatives, R_3SnX , yielding $[\text{R}_3\text{Sn}(\text{Dn})_2][\text{X}]$ has previously been shown for $[\text{Bu}_3\text{Sn}(\text{HMPA})_2][\text{ClO}_4]$,³⁹ $[\text{Ph}_3\text{Sn}(\text{HMPA})_2][\text{ClO}_4]$,³⁹ $[(\text{CH}_3)_3\text{Sn}(\text{O}=\text{S}(\text{CH}_3)_2)[\text{N}(\text{SO}_2\text{F})_2]$,¹⁷ and $[(\text{CH}_3)_3\text{Sn}(\text{py})_2][\text{N}(\text{SO}_2\text{F})_2]$ ¹⁷ in solution and was found in the present work for $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ in the solid state by X-ray crystallography (see Crystal Structures (b)).

(b) $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$. Nuclear magnetic resonance spectroscopic data for $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ in CH_2Cl_2 and $(\text{CH}_3)_2\text{CO}$ solvents are listed in the experimental section. In

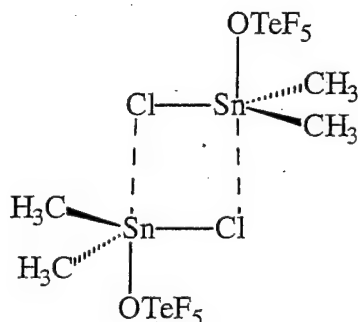
both solvents, two sets of signals were observed. At room temperature, the tin signals are broadened to ca 300 and ca 3300 Hz in CH_2Cl_2 and $(\text{CH}_3)_2\text{CO}$ solutions, respectively. At 223 K the linewidth for the ^{119}Sn resonances in CH_2Cl_2 decreased somewhat and their relative intensities change compared to those recorded at room temperature indicating that an equilibrium is operational, whose nature is presently not understood. In CH_2Cl_2 solvent, the ^{119}Sn resonances appear at 127 and 143 ppm which is in the chemical shift range for tetracoordinate dimethyltin. As observed for $(\text{CH}_3)_3\text{SnOTeF}_5$ (vide supra), dissolution in donor solvents such as $(\text{CH}_3)_2\text{CO}$ results in an increase in ^{119}Sn shieldings to 33 and -79 ppm which is consistent with pentacoordinate tin. In CH_2Cl_2 solution, two separate sets of ^1H , ^{13}C , ^{19}F , and ^{119}Sn NMR signals could be distinguished. At low temperature a second set of ^{125}Te NMR signals was resolved. Small deviations in chemical shifts and coupling constants between the two sets indicate similar geometries of the two species present in solution. In $(\text{CH}_3)_2\text{CO}$, two very broad ^{119}Sn resonances could be distinguished. The NMR spectroscopic parameters of the OTeF_5 in both solvents are similar to those for neat $(\text{CH}_3)_3\text{SnOTeF}_5$ (vide supra) indicating that the Sn-O bond has not been cleaved in those solution.

The C-Sn-C angles for $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ in various solvents can be calculated from the $^2J(^{119}\text{Sn}-^1\text{H})$ coupling constants using equation (9), as recommended by Lockhart³⁷ for

$$\theta = 0.0105 [^2J(^{119}\text{Sn}-^1\text{H})]^2 - 0.799 [^2J(^{119}\text{Sn}-^1\text{H})] + 122.4 \quad (9)$$

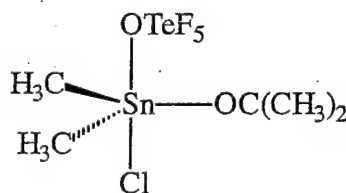
dimethyl tin compounds with highly electronegative substituents. The C-Sn-C angle calculated using $^2J(^{119}\text{Sn}-^1\text{H})$ and $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants for $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ dissolved in CH_2Cl_2 is approximately $\sim 118^\circ$. The $\delta(^{119}\text{Sn})$ value of ~ 120 ppm indicates that tin is present in a

five-coordinate environment. The fifth coordination site is most likely occupied by a bridging chlorine ligand from a second $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$ molecule, as shown below:



Such a pseudo-trigonal bipyramidal structure could account for the increase of the C-Sn-C angle from a tetrahedral value of 109.5° to about 120° . The proposed structure is similar to the one found in the solid-state structure of $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$ as shown in Fig.1.

In acetone, an increase in the $^2J(^{119}\text{Sn}-^1\text{H})$ and $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants values by ~ 21 and ~ 220 Hz, respectively, results in the calculated C-Sn-C angle increases to 137° , compared to the values found in CH_2Cl_2 solution indicating the formation of a distorted trigonal bipyramidal adduct:



(c) $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$. For the $\text{N}(\text{SO}_2\text{F})_2$ ligand, the fluorine chemical shifts provide a mean to distinguish ionic and covalent $\text{N}(\text{SO}_2\text{F})_2$ moieties. Typical $\delta(^{19}\text{F})$ values for covalent derivatives lie around 55.5 ppm and for ionic derivatives, the resonance is more shielded by ca 3 ppm to 52.5 ppm.¹⁷ However, in the case of the $\text{N}(\text{SO}_2\text{CF}_3)_2$ group, the fluorine

atoms are isolated by greater bond separation and, therefore, do not show any significant chemical shift difference between ionic and covalent derivatives.¹⁸

The ¹¹⁹Sn chemical shifts for [(CH₃)₃Sn(H₂O)₂][N(SO₂CF₃)₂] in CH₃CN and DMSO are 59.0 and 42.8 ppm, which are more shielded by ca 200 ppm compared to that of neat (CH₃)₃SnN(SO₂CF₃)₂.¹⁸ This low-frequency shift confirms the presence of a pentacoordinate tin species, which is either the (CH₃)₃Sn(H₂O)₂⁺ cation that was found in the solid state, or cationic species with partially or completely displaced water molecules, i.e., (CH₃)₃Sn(H₂O)(Dn)⁺ or (CH₃)₃Sn(Dn)₂⁺, with Dn = CH₃CN and DMSO.

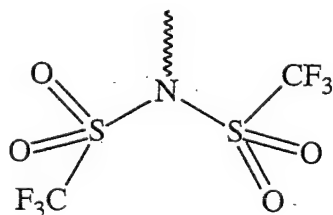
Crystal Structures Details of the data collection and other crystallographic information for (CH₃)₂SnCl(OTeF₅) and [(CH₃)₃Sn(H₂O)₂][N(SO₂CF₃)₂] are given in Table 3. Bond lengths and bond angles for (CH₃)₂SnCl(OTeF₅) and [(CH₃)₃Sn(H₂O)₂][N(SO₂CF₃)₂] are given in Table 4 and 5, respectively.

(a) (CH₃)₂SnCl(OTeF₅). The crystal structure of (CH₃)₂SnCl(OTeF₅), which crystallizes in the monoclinic system, contains (CH₃)₂SnCl(OTeF₅) molecules with distorted tetrahedral coordination about tin and a Sn-Cl distance of 2.386(1) Å, which is the same as 2.388(4) Å found in the crystal structures of (C₂H₅)₂SnCl(OOCH₃).¹⁵ The OTeF₅ group is tilted towards one methyl group (C(2)) resulting in a widening of the O(1)-Sn(1)-C(2) angle (105.04(15)°) compared to the O(1)-Sn(1)-C(1) (95.44(14)°) and O(1)-Sn(1)-Cl(1) (94.64(17)°) angles.

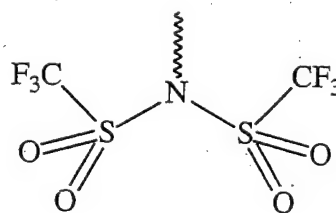
The coordination sphere around tin is extended by a contact to Cl to a trigonal bipyramid (Fig.1). A chlorine atom of one (CH₃)₂SnCl(OTeF₅) molecule coordinates through the tetrahedral face formed by chlorine and two carbon atoms, located at its vertices, of a second molecule, and vice versa, resulting in dimer formation Fig (1). These symmetry related contacts of 3.201(1) Å [Sn...Cl(1B) (2-x, 1-y, -z)] are significantly smaller than the sum of the van der Waals radii (3.91

Å)⁴⁰ (Table 3). The Sn...Cl contacts in (CH₃)₂SnCl(OTeF₅) are similar to those in the chlorine-bridged methyltin(IV) derivatives, ((CH₃)₂SnCl)₂ (3.240(3) and 3.292(3) Å)⁴¹ and (CH₃)₃SnCl (3.269(2) Å),⁷ however, they are significantly shorter than those in (C₂H₅)₂SnCl(OOCCH₃) (3.875 Å),¹⁵ bis(μ²-chloro)chlorodimethyltin-(diphenylcyclopropenone-o)tin(IV) (3.561 Å),⁴² and (C₆H₅)₂SnCl₂ (3.872 Å).⁴³ In addition to the Sn...Cl contacts, one fluorine atom of an OTeF₅ group exhibits a Sn...F(2) (1+x, y, z) contact with 3.141(3) Å (Σr_{vdw}(Sn-F) = 3.64 Å),⁴⁰ occupying the fourth corner of the square plane around tin, the other three being occupied by O(1), Cl(1) and Cl(1B) (2-x, 1-y, -z) and extending the coordination number about tin to six. No long-range contacts are observed from the oxygen atom of the OTeF₅ group implying that this anion shows no bridging via the oxygen atom. The crystal packing can be seen as a sheet-like polymeric structure containing chains with the Sn...F(2) contacts bridging the dimeric units (Fig. 2).

(b) [(CH₃)₃Sn(H₂O)₂][N(SO₂CF₃)₂]. The crystal structure of [(CH₃)₃Sn(H₂O)₂][N(SO₂CF₃)₂] contains separated (CH₃)₃Sn(H₂O)₂⁺ cations and N(SO₂CF₃)₂⁻ anions which are shown in Figure 3. This structure is similar to that observed for [(CH₃)₃Sn(H₂O)₂][N(SO₂CH₃)₂].⁴⁴ The tin atom is present in a trigonal bipyramidal structure with the three methyl groups in the equatorial positions, and the axial positions being occupied by the two water molecules with Sn-O distances of 2.306(3) and 2.335(3) Å. The trifluoromethyl groups on the N(SO₂CF₃)₂ anion can be present in the *cis*- or *trans*-conformation:



Trans



Cis

In the case of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CH}_3)_2]$, the trifluoromethyl groups are oriented in a *trans*-manner with respect to each other. This orientation is most favored and is found in the structures of $\text{HN}(\text{SO}_2\text{CF}_3)_2$,^{45,46} $[\text{Mg}(\text{H}_2\text{O})_6][\text{N}(\text{SO}_2\text{CF}_3)_2]$,⁴⁵ $[\text{Cu}(\text{CO})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$,⁴⁷ and 1-ethyl-2-methyl-3-benzyl-imidazolium bis(trifluoromethylsulfonyl)imide.⁴⁸ However, the *cis*-conformation has been observed in the case of $\text{KN}(\text{SO}_2\text{CF}_3)_2$.⁴⁶ The S-N distances of 1.589(3) and 1.573(3) Å are relatively short when compared to those reported for $\text{HN}(\text{SO}_2\text{CF}_3)_2$ of 1.644(1)⁴⁵ and 1.647 Å⁴⁶ and the S-N-S angle is compressed from 128.4(2)⁴⁵ in $\text{HN}(\text{SO}_2\text{CF}_3)_2$ to 125.3(2)° in the present compound. However, the latter value is significantly greater than the corresponding S-N-S angle of 121.5(2)° in the case of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CH}_3)_2]$.⁴⁴ The crystal-packing diagram along the *c*-axis (Fig. 4) shows a three-dimensional hydrogen-bonding network in the *ab*-plane. The $\text{O}\cdots\text{H}$ ($x, \frac{1}{2} - y, \frac{1}{2} + z$) contacts range from 1.95 to 2.60 Å showing a tightly packed crystal lattice due to hydrogen bonding. A bifurcated hydrogen bond is formed from $\text{O}(1)\text{-H}(11)\cdots\text{O}(4)$ and $\text{O}(1)\text{-H}(11)\cdots\text{O}(5)$ at 2.16(5) and 2.60(5) Å ($x, \frac{1}{2} - y, \frac{1}{2} + z$), respectively. There is also a short contact resulting from one of the hydrogen atoms from a water molecule, $\text{O}(2)\text{-H}(21)$ and the nitrogen atom of the $\text{N}(\text{SO}_2\text{CF}_3)_2$ group, i.e., $\text{N}(1)\cdots\text{H}(21)$ ($-1 + x, y, z$) at 2.17(6) Å.

Conclusions

In the present study, the $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ was prepared by reacting $(\text{CH}_3)_3\text{SnCl}$ with HOTeF_5 or ClOTeF_5 where the Sn-C bond is cleaved, and it represents the first structurally characterized methyl tin(IV) pentafluorooxotellurate. Multi-NMR spectroscopy of $(\text{CH}_3)_3\text{Sn}(\text{OTeF}_5)$ in various solvents revealed the strong dependence of the coordination

environment of the tin(IV) species in solution on the donor strength of the solvent. In DMSO, the strongest donor solvent studied, the dissociation of the Sn-OTe bond was facilitated with formation of $[(\text{CH}_3)_3\text{Sn}(\text{O}=\text{S}(\text{CH}_3)_2)_2][\text{OTeF}_5]$. The crystal structure of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ unambiguously proves the existence of such solvated salts in the solid state and represents only the second crystal structure of such a solvated tin(IV) salt.

Experimental

Materials and Apparatus. Reactions were carried out in Teflon-FEP or -PFA ampoules that contained Teflon coated magnetic stirring bars and were closed by stainless steel valves. Volatile materials were handled either on a stainless steel/Teflon-FEP vacuum line⁴⁹ or a Pyrex glass vacuum line equipped with grease-free Kontes glass-Teflon valves. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box.

The $(\text{CH}_3)_3\text{SnCl}$ and $\text{Sn}(\text{CH}_3)_4$ (Aldrich Chemical Co.) were used as received. The HOTeF_5 was prepared from either CsOTeF_5 (Rocketdyne) or pyHOTeF_5 (kindly supplied by Prof. Steve Strauss, Colorado State University) after its reaction with concentrated H_2SO_4 , and purified by fractional condensation at -78°C over -45°C . The ClOTeF_5 was generated by the reaction of HOTeF_5 with an excess of ClF , followed by purification via fractional condensation at -95°C over -78°C . $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ was prepared as described earlier¹⁸ and CFCl_3 (Matheson) was dried by storage over P_4O_{10} before use.

Infrared and Raman Spectroscopy. Infrared spectra were recorded on a Mattson Galaxy 5030 FT-IR spectrometer using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on either a Bruker Equinox 55 FT-RA spectrometer using a Nd-Yag laser at 1064 nm and Pyrex melting point

capillaries as sample containers or a Cary Model 83 spectrometer using the 488 nm exciting line of an Ar ion laser.

NMR Spectroscopy. The NMR spectra were recorded at 500.13 MHz (^1H), 470.51 MHz (^{19}F), 125.76 MHz (^{13}C), 186.50 MHz (^{119}Sn) and 158.03 MHz (^{125}Te) on a Bruker AMX 500 or at 400.13 MHz (^1H), 376.54 MHz (^{19}F), 100.62 MHz (^{13}C), 149.22 MHz (^{119}Sn) and 126.45 MHz (^{125}Te) on a Bruker Avance 400 NMR spectrometer using neat liquid/solutions in a sealed standard glass tube. The following external references were used: ^1H and ^{13}C : neat TMS (0 ppm); ^{19}F : neat CFCl_3 (0 ppm); ^{119}Sn : neat $\text{Sn}(\text{CH}_3)_4$ (0 ppm); ^{125}Te : a saturated aqueous $\text{Te}(\text{OH})_6$ solution (710.9 ppm).⁵⁰ The AB_4 spin patterns in the ^{19}F NMR spectra were simulated using the program gNMR.⁵¹

Mass Spectrometry. The mass spectrometric data were collected on a Jeol JMS AX505HA or a HP Agilent 6890 GC Mass spectrometer using the EI method. The isotopic pattern were simulated using a shareware software.⁵²

X-ray Crystallography. The single crystal X-ray diffraction data were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the χ -axis fixed at 54.74° and using MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine-focus tube. This diffractometer was equipped with an LT-3 apparatus for low temperature data collection using controlled liquid nitrogen boil off. The goniometer head, equipped with a Nylon Cryoloop with a magnetic base, was then used to mount the crystals using PFPE (perfluoropolyether) oil and mounted on the magnetic goniometer. Cell constants were determined from 90 thirty-second frames at $\sim 215 \text{ K}$ (see Table 3). A complete hemisphere of data was scanned on omega (0.3°) with a run time of thirty-second per frame at a detector resolution of 512×512 pixels using the SMART software.⁵³ A total of 1271 frames were

collected in three sets and final sets of 50 frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC running on Windows NT software by using the SAINT software⁵⁴ to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS⁵⁵ program. The structures were solved by the direct method using the SHELX-90⁵⁶ program and refined by the least squares method on F^2 , SHELXL-97⁵⁷ incorporated in SHELXTL Suite 5.10 for Windows NT.⁵⁸ All non-hydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. The methyl-hydrogen atoms in $(CH_3)_2SnCl(OTeF_5)$ and $[Me_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ were added at calculated positions while hydrogen atoms of the water molecules were located and refined isotropically from electron density maps.

Preparation of $(CH_3)_2SnCl(OTeF_5)$. Inside the drybox, $(CH_3)_3SnCl$ (1.3740 g, 6.8952 mmol) was loaded into a Teflon ampoule, followed by the addition of $HOTeF_5$ (1.8057 g, 7.5363 mmol) *in vacuo* at $-196^\circ C$. The reactants were allowed to warm to room temperature for 12 hours. When the volatile components were removed from the ampoule and collected at $-196^\circ C$, the only volatile by-product identified by infrared spectroscopy was CH_4 (besides some unreacted $HOTeF_5$). Further reaction for three hours at $60^\circ C$, followed by removal of all volatiles and subsequent sublimation, yielding a white solid in 73.2% yield that was identified by vibrational and multi-NMR spectroscopy and X-ray crystallography as $(CH_3)_2SnCl(OTeF_5)$.

Alternatively, a Teflon FEP ampoule was loaded with $ClOTeF_5$ (0.6702 g, 2.445 mmol) *in vacuo* at $-196^\circ C$ followed by condensation of $CFCl_3$ solvent (3.1645 g) onto the $ClOTeF_5$. Inside the drybox, $(CH_3)_3SnCl$ (0.4883 mg, 2.450 mmol) was then added at $-196^\circ C$ to the frozen solution. After evacuating the ampoule at $-196^\circ C$, the ampoule was warmed to room

temperature for 1-1/2 h. The volatile components were removed under dynamic vacuum at room temperature and CH_3Cl was identified as the only volatile component besides CFCl_3 solvent via infrared spectroscopy. A white solid (0.7552 g) was isolated after removal of all volatile material in 72.7% crude yield. This solid was further purified by sublimation at $\sim 50^\circ\text{C}/0.001$ Torr, and identified as $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ by vibrational spectroscopy. Spectroscopic data obtained are as follows: **IR (AgCl), cm^{-1} :** 3041w ($\nu_{\text{as}}\text{CH}_3$), 2941 w, ($\nu_{\text{s}}\text{CH}_3$), 1406 mw, 1314 w, 1284 w, 1210 mw, 1019 m, 860 vs (νTeO), 811 vs (ρCH_3), 693 vs ($\nu\text{TeF}_{\text{eq}}$), 617 ms ($\nu\text{TeF}_{\text{ax}}$), 580 mw ($\nu_{\text{as}}\text{Sn-C}$), 524 m ($\nu_{\text{s}}\text{Sn-C}$), 426 ms. **Raman, cm^{-1} (rel. int.):** 3024 (8); 2941 sh; 2925 (47); 1208 (18); 1186 (2); 857 (3); 702 (7); 686 (5); 629 (8); 616 (4); 581 (5); 568 (10); 518 (100); 423 (3); 313 (53); 229 (5); 179 (30); 143 (24); 119 (23). **MS (EI) major ^{120}Sn fragments** (pattern matches simulated spectra): 409 $[\text{M} - \text{CH}_3]^+$ 85, 389 $[(\text{CH}_3)_2\text{SnOTeF}_5]^+$ 61, 169 $[(\text{CH}_3)_2\text{SnF}]^+$ 100. **NMR spectroscopic data; acetone- d_6 solvent at 300 K:** $\delta(^1\text{H}) = 1.73$ ppm, s, $^1J(^{13}\text{C}-^1\text{H}) = 136.7$ Hz, $^2J(^{117/119}\text{Sn}-^1\text{H}) = 87.4/91.3$ Hz, $\Delta\nu_{1/2} = 1.5$ Hz; $\delta(^{13}\text{C}) = 12.46$ ppm, s, $^1J(^{117/119}\text{Sn}-^{13}\text{C}) = 659.5/695.1$ Hz, $\Delta\nu_{1/2} = 17.8$ Hz; $\delta(^{119}\text{Sn}) = -79.3$ ppm, $\Delta\nu_{1/2} = 3220$ Hz; $\delta(^{119}\text{Sn}) = 33.2$ ppm, $\Delta\nu_{1/2} = 3350$ Hz; $\delta(^{125}\text{Te}) = 572.56$ ppm, d of quint., $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{eq}}) = 3553.4$ Hz, $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{ax}}) = 3088.4$ Hz, $\Delta\nu_{1/2} = 53.3$ Hz. **CH_2Cl_2 solvent at 300 K:** $\delta(^1\text{H}) = 0.61$ ppm, s, $^2J(\text{Sn}-^1\text{H}) = 67.9$ Hz, $\Delta\nu_{1/2} = 23.7$ Hz; $\delta(^{13}\text{C}) = 7.49$ ppm, s, $^1J(\text{Sn}-^{13}\text{C}) = 472$ Hz, $\Delta\nu_{1/2} = 50$ Hz; $\delta(^{19}\text{F}_{\text{ax}}) = -36.45$ ppm, $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{ax}}) = 3325$ Hz, $^2J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}}) = 182$ Hz; $\delta(^{19}\text{F}_{\text{eq}}) = -41.15$ ppm, $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{eq}}) = 3551$ Hz; $\delta(^{119}\text{Sn}) = 127.3$ ppm, $\Delta\nu_{1/2} = 302$ Hz; $\delta(^{125}\text{Te}) = 576.13$ ppm, d of quint., $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{eq}}) = 3551$ Hz, $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{ax}}) = 3325$ Hz, $\Delta\nu_{1/2} = 271.8$ Hz. Minor component: $\delta(^1\text{H}) = 0.47$ ppm, s, $^2J(\text{Sn}-^1\text{H}) = 70$ Hz, $\Delta\nu_{1/2} = 33.2$ Hz; $\delta(^{13}\text{C}) = 6.48$ ppm, s, $\Delta\nu_{1/2} = 66$ Hz; $\delta(^{19}\text{F}_{\text{ax}}) = -34.90$ ppm, $^2J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}}) = 182$ Hz; $\delta(^{19}\text{F}_{\text{eq}}) = -40.17$ ppm, $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{eq}}) = 3554$ Hz; $\delta(^{119}\text{Sn}) = 142.7$ ppm, $\Delta\nu_{1/2} = 313$ Hz. Ratio major:minor component based on integrals of the

^{119}Sn resonances: 2.4 : 1.0. $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ in CH_2Cl_2 solvent at 223 K : $\delta(^1\text{H}) = 0.39$ ppm, s, $^2J(\text{Sn}-^1\text{H}) = 68.4$ Hz, $\Delta\nu_{1/2} = 12.8$ Hz; $\delta(^{13}\text{C}) = 7.49$ ppm, s, $^1J(\text{Sn}-^{13}\text{C}) = 474.3$ Hz, $\Delta\nu_{1/2} = 12.1$ Hz; $\delta(^{119}\text{Sn}) = 140.23$ ppm, sept., $^2J(^{119}\text{Sn}-^1\text{H}) = 70.6$ Hz, $\Delta\nu_{1/2} = 51$ Hz; $\delta(^{125}\text{Te}) = 575.53$ ppm, d of quint., $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{eq}}) = 3570.6$ Hz, $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{ax}}) = 3276.8$ Hz, $\Delta\nu_{1/2} = 112$ Hz. Minor component: $\delta(^1\text{H}) = 0.25$ ppm, s, $^2J(\text{Sn}-^1\text{H}) = 68.0$ Hz, $\Delta\nu_{1/2} = 11.4$ Hz; $\delta(^{13}\text{C}) = 8.76$ ppm, s, $^1J(\text{Sn}-^{13}\text{C}) = 482.2$ Hz, $\Delta\nu_{1/2} = 12.2$ Hz; $\delta(^{119}\text{Sn}) = 114.7$ ppm, $^2J(^{119}\text{Sn}-^1\text{H}) \approx 65$ Hz, $\Delta\nu_{1/2} = 243$ Hz; $\delta(^{125}\text{Te}) = 577.48$ ppm, d of quint., $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{eq}}) = 3562.9$ Hz, $^1J(^{125}\text{Te}-^{19}\text{F}_{\text{ax}}) = 3306.7$ Hz, $\Delta\nu_{1/2} = 97$ Hz. Ratio major:minor component based on integrals of the ^{119}Sn resonances: 1.3 : 1.0.

Preparation of $(\text{CH}_3)_3\text{Sn}(\text{OTeF}_5)$. After condensation of HOTeF_5 (0.8428 g, 3.518 mmol) into a Teflon ampoule via a stainless steel vacuum line at -196°C , excess $\text{Sn}(\text{CH}_3)_4$ (3.1144 g, 17.429 mmol) was added to the ampoule on a glass vacuum line in vacuo at -196°C . A brisk effervescence was observed upon slowly warming the reaction mixture to room temperature over a period of 45 min. The volatile components were then removed in vacuo at $\sim 20^\circ\text{C}$, leaving behind a clear colorless liquid ($(\text{CH}_3)_3\text{Sn}(\text{OTeF}_5)$; 1.3819 g; 3.434 mmol). Inspection of the volatile material trapped at -196°C by gas-phase infrared spectroscopy showed methane as the sole reaction by-product. The colorless liquid, $(\text{CH}_3)_3\text{Sn}(\text{OTeF}_5)$, was characterized by vibrational spectroscopy and multi-NMR spectroscopy. Spectroscopic data obtained are as follows: **IR (AgCl), cm^{-1} :** 3009 w ($\nu_{\text{as}}\text{CH}_3$), 2929 w, ($\nu_{\text{s}}\text{CH}_3$), 1402 w, 1296 w, 1202 mw, 860 s (νTeO), 789 s (ρCH_3), 688 vs ($\nu\text{TeF}_{\text{eq}}$), 613 mw ($\nu\text{TeF}_{\text{ax}}$), 552 ms ($\nu_{\text{as}}\text{Sn-C}$), 518 m ($\nu_{\text{s}}\text{Sn-C}$), 429 ms. **Raman, cm^{-1} (rel. int):** 3008 (7); 2930 (14); 1214 (6), 1204 sh; 856 (4), 781 (<1); 681 (72); 624 (4); 554 (16); 518 (100); 431 (4); 334 (5); 296 (4); 230 (4); 146 (22). **MS (EI):** major ^{120}Sn fragments (pattern matches simulated spectra): 389 [$(\text{CH}_3)_2\text{SnOTeF}_5$] $^+$ 46, 169 [$(\text{CH}_3)_2\text{SnF}$] $^+$ 100.

Preparation of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$. A solution of $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ in CH_2Cl_2 (0.25g in 5 mL) was added to ca 10 mL of chloroform that was presaturated with water. The mixture was stirred for 30 min and then left undisturbed for ca 48 h inside a fume hood. During this time colorless crystals had formed which were isolated, washed with cold CH_2Cl_2 and dried in vacuo. The vibrational data obtained are as follows: **IR (AgCl), cm^{-1} :** 3470 vs, br (vOH), 2996 sh ($\nu_{\text{as}}\text{CH}_3$), 2929 w, ($\nu_{\text{s}}\text{CH}_3$), 1614 vs (vOH), 1346 vs, 1201 vs, 1133 vs, 1053 vs, 797 vs ($\nu_{\text{as}}\text{SNS}$), 742 ($\nu_{\text{s}}\text{SNS}$), 616 vs, 572 s, 514 s ($\nu_{\text{s}}\text{Sn-C}$). **Raman, cm^{-1} (rel. int):** 2928 (32); 1242 (18); 1218 (11); 1132 (12); 746 (44); 560 (21); 523 (100); 401 (6); 342 (6); 316 (4); 277 (10); 157 (13); 140 (13), 119 sh.

NMR studies in donor solvents. Approximately 100 mg of $(\text{CH}_3)_3\text{SnOTeF}_5$ was loaded into a 5-mm glass NMR tube inside a glove box. The tube was sealed with a rubber septum and ca 0.5 mL of solvent was injected into the NMR tube via the septum prior to inserting the tube into the probe. When samples were prepared with aqueous acetonitrile/DMSO, white precipitates started forming within minutes, indicating the decomposition of the OTeF_5 group, as seen by the appearance of many complex signals in the ^{19}F and ^{125}Te NMR spectra. In the case of $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$, NMR samples were prepared in side a dry box by loading approximately 50 mg of $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ into a 5-mm glass NMR tube connected to a Kontes valve via a Cajon Ultratorr union. Subsequently, ca 0.5 mL of anhydrous solvent was vacuum distilled onto the solid, followed by flame sealing of the NMR tube. The samples were stored at $-196\text{ }^\circ\text{C}$ until their NMR spectroscopic characterization.

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Table 1. ^1H , ^{13}C NMR Spectroscopic Data^a and calculated^{b,c} C-Sn-C angles for $(\text{CH}_3)_3\text{SnX}$ [$\text{X} = \text{OTeF}_5$ and $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$]

Solute	Solvent ^d	$\delta(^1\text{H})$ ppm	$^2J(^{119}\text{Sn}-^1\text{H})$ Hz	$\theta(\text{C-Sn-C})^b$ ($^\circ$)	$\delta(^{13}\text{C})$ ppm	$^1J(^{119}\text{Sn}-^{13}\text{C})$ Hz	$\theta(\text{C-Sn-C})^c$ ($^\circ$)	Ref
$(\text{CH}_3)_3\text{SnOTeF}_5$	neat	0.84	59.2 ^e	111.7	0.84	376.9(360.3)	109.8	This work
	CH_2Cl_2	0.79	58.5(55.9)	111.3	0.90	374.0(357.4)	109.6	This work
	acetone	0.69	68.8(65.8)	118.8	1.55	480.4(459.3)	118.9	This work
	CH_3CN	0.66	69.2(66.2)	119.2	1.49	484.6(463.1)	119.3	This work
	DMSO	0.50	69.5(66.6)	119.4	1.05	511.4(490.0)	121.6	This work
$(\text{CH}_3)_3\text{SnOTeF}_5$	$\text{AN}/\text{H}_2\text{O}$	0.46	69.6(66.7)	119.5	0.10	508.5(486.0)	121.4	This work
	DMSO/ H_2O	0.43	70.1(68.5) ^e	120.0	0.84	515.5(492.5)	122.0	This work
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat	0.91	63.8(61.6)	114.7	1.6	416.8(400.3)	113.3	17
	CH_2Cl_2	0.96	62.3(59.9)	113.6	1.4	404.1(387.7)	112.2	17
	DMSO	0.83	72.4(70.0)	122.2	-0.2	528.3(509.9)	123.1	17
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$	neat	0.84	64.2(61.6)	115.0	2.1	412.6(394.1)	113.0	18
	CH_2Cl_2	0.81	64.4(61.8)	115.2	0.8	414.8(395.2)	113.0	18
	CH_3CN	0.82	70.2(67.1)	120.1	-1.7	489.5(467.6)	119.7	18
	DMSO	0.48	69.0(67.4)	119.0	0.7	512.2(499.0)	121.6	18
	$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	0.61	69.7(66.7)	119.6	0.10	491.8(470.0)	120.0	This work
	DMSO	1.18	69.8(66.7)	119.7	0.92	512.9(497.2)	121.8	This work

^a NMR spectroscopic data were recorded at 300 K.

^b Calc from relation: $\theta = 0.0161 [^2J(^{119}\text{Sn}-^1\text{H})]^2 - 1.32 [^2J(^{119}\text{Sn}-^1\text{H})] + 133.4$.

^c Calc from relation: $[^1J(^{119}\text{Sn}-^{13}\text{C})] = 11.4 \theta - 875$.

^d Acetone = $(\text{CD}_3)_2\text{CO}$, DMSO = $(\text{CD}_3)_2\text{SO}$.

^e Calculated from center of unresolved ^{119}Sn , ^{117}Sn satellites ($|J_{\text{obs}}| \times 1.023$).²⁸

Table 2. ^{19}F , ^{119}Sn and ^{125}Te NMR Spectroscopic Data^a of $(\text{CH}_3)_3\text{SnX}$ [$\text{X} = \text{OTeF}_5$ and $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$]

Solute	Solvent ^b	$\delta(^{19}\text{F})$, ppm		$^2J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}})$, Hz		$\delta(^{119}\text{Sn})$, ppm	$\delta(^{125}\text{Te})$, ppm	$\delta(^{13}\text{CF}_3)$, ppm	$^1J(^{125}\text{Te}-^{19}\text{F})$, Hz		$^1J(^{13}\text{C}-^{19}\text{F})$, Hz	Ref.
		F_{ax}	F_{eq}	$\text{CF}_3/\text{SO}_2\text{F}$	Hz				F_{ax}	F_{eq}		
$(\text{CH}_3)_3\text{SnOTeF}_5$	neat	-32.9	-41.9		182.5	270.8	569.5		3112	3540		This work
	CH_2Cl_2	-30.3	-38.5		183.0	272.4	564.6		3188	3550		This work
	acetone	-29.1	-40.6		180.0	96.0	574.9		3020	3558		This work
	CH_3CN	-29.2	-40.8		179.0	84.2	575.0		3032	3556		This work
	DMSO	-16.2	-33.8		170.0	40.0	598.7		2712	3666		This work
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat			55.5		242.5						16
	CH_2Cl_2			55.6		248.6						16
	DMSO			52.5		32.9						16
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$	neat			-78.5		240.2		118.7			320.4	17
	CH_2Cl_2			-78.8		251.0		118.1			319.8	17
	CH_3CN			-78.9		44.9		119.4			320.7	17
	DMSO			-78.6		37.4		120.0			321.7	17
$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	CH_3CN			-79.0		59.0						This work
	DMSO			-79.1		42.8						This work

^a NMR spectroscopic data were recorded at 300 K.

^b Acetone = $(\text{CD}_3)_2\text{CO}$, DMSO = $(\text{CD}_3)_2\text{SO}$.

Table 3. Crystal data and structure refinement for (CH₃)₂SnCl(OTeF₅) and [(CH₃)₃Sn(H₂O)₂][N(SO₂CF₃)₂]

Empirical formula	C ₂ H ₆ ClF ₅ OSnTe	C ₅ H ₁₃ F ₆ NO ₆ S ₂ Sn
Formula weight	422.81	479.97
T, K	218(2)	213(2)
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions <i>a</i> , Å	5.8204(8)	7.3072(1)
<i>b</i> , Å	10.782(1)	13.4649(2)
<i>c</i> , Å	15.493(2)	16.821(2)
β , °	91.958(2)	98.705(1)
Volume, Å ³	971.7(2)	1636.00(3)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	2.890	1.949
Absorption coefficient (mm ⁻¹)	5.872	1.898
Theta for data (°)	2.30 to 29.30	1.95 to 28.27
Goodness-of-fit on <i>F</i>	1.088	1.233
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0282, 0.0712	0.0367, 0.0736
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0333, 0.0743	0.0410, 0.0759

$$R1 = (\Sigma(F_o - F_c)/F_o); wR2 = [\Sigma(w(F_o - F_c)^2)/wF_o^2]^{1/2}$$

Table 4. Bond lengths [Å] and angles [°] for (CH₃)₂SnCl(OTeF₅)

Bond Lengths and Contacts

Sn(1)-O(1)	2.065(3)	Te(1)-F(5)	1.815(3)
Sn(1)-C(2)	2.094(4)	Te(1)-F(4)	1.819(3)
Sn(1)-C(1)	2.094(4)	Te(1)-F(1)	1.831(3)
Sn(1)-Cl(1)	2.3858(11)	Te(1)-F(3)	1.843(3)
O(1)-Te(1)	1.803(3)	Te(1)-F(2)	1.849(3)

Bond Angles

O(1)-Sn(1)-C(2)	105.04(15)	F(5)-Te(1)-F(1)	86.50(14)
O(1)-Sn(1)-C(1)	95.44(14)	F(4)-Te(1)-F(1)	90.65(16)
C(2)-Sn(1)-C(1)	139.05(17)	O(1)-Te(1)-F(3)	94.68(13)
O(1)-Sn(1)-Cl(1)	94.64(9)	F(5)-Te(1)-F(3)	86.48(14)
C(2)-Sn(1)-Cl(1)	106.63(13)	F(4)-Te(1)-F(3)	90.54(17)
C(1)-Sn(1)-Cl(1)	106.58(13)	F(1)-Te(1)-F(3)	172.81(12)
Te(1)-O(1)-Sn(1)	137.59(17)	O(1)-Te(1)-F(2)	93.38(14)
O(1)-Te(1)-F(5)	178.67(15)	F(5)-Te(1)-F(2)	85.99(16)
O(1)-Te(1)-F(4)	93.57(15)	F(4)-Te(1)-F(2)	173.05(14)
F(5)-Te(1)-F(4)	87.06(16)	F(1)-Te(1)-F(2)	88.89(14)
O(1)-Te(1)-F(1)	92.33(12)	F(3)-Te(1)-F(2)	89.06(16)

Table 5. Bond lengths [Å] and angles [°] for $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$

Bond Lengths and Contacts

Sn(1)-C(2)	2.104(4)	S(1)-N(1)	1.573(3)
Sn(1)-C(1)	2.115(4)	S(1)-C(4)	1.825(5)
Sn(1)-C(3)	2.120(4)	S(2)-O(6)	1.421(3)
Sn(1)-O(1)	2.306(3)	S(2)-O(5)	1.433(3)
Sn(1)-O(2)	2.335(3)	S(2)-N(1)	1.589(3)
S(1)-O(3)	1.427(2)	S(2)-C(5)	1.844(4)
S(1)-O(4)	1.428(3)		

Bond Angles

C(2)-Sn(1)-C(1)	117.8(2)	O(3)-S(1)-N(1)	107.6(2)
C(2)-Sn(1)-C(3)	120.1(2)	O(4)-S(1)-N(1)	116.1(2)
C(1)-Sn(1)-C(3)	122.1(2)	O(3)-S(1)-C(4)	104.0(2)
C(2)-Sn(1)-O(1)	89.83(15)	O(4)-S(1)-C(4)	105.4(2)
C(1)-Sn(1)-O(1)	92.3(2)	O(6)-S(2)-O(5)	118.2(2)
C(3)-Sn(1)-O(1)	87.19(13)	O(6)-S(2)-N(1)	109.0(2)
C(2)-Sn(1)-O(2)	91.04(15)	O(5)-S(2)-N(1)	115.3(2)
C(1)-Sn(1)-O(2)	90.8(2)	O(6)-S(2)-C(5)	104.7(2)
C(3)-Sn(1)-O(2)	88.95(13)	O(5)-S(2)-C(5)	105.0(2)
O(1)-Sn(1)-O(2)	175.94(11)	S(1)-N(1)-S(2)	125.3(2)
O(3)-S(1)-O(4)	118.5(2)		

- Figure 1 DIAMOND plot of $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ showing the dimmer formation via $\text{Sn}\cdots\text{Cl}$ contacts. The thermal ellipsoids are at 30% probability.
- Figure 2 The unit cell along the *b*-axis of $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ showing extended $\text{Sn}\cdots\text{Halogen}$ contacts.
- Figure 3 DIAMOND plot showing the trigonal bipyramidal geometry of the $(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2^+$ cation and the *trans*-conformation of the $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ anion with thermal ellipsoids at 50% probability level.
- Figure 4 Crystal packing diagram of $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ showing the hydrogen bonding network.

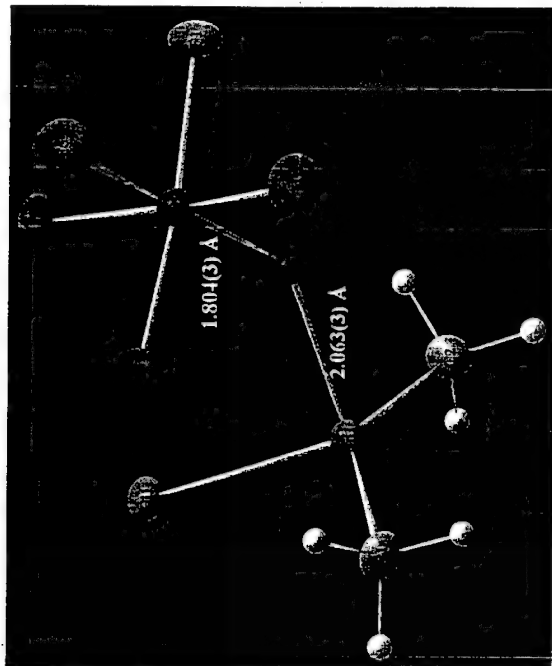
Graphical Abstract

Methyl Tin(IV) Derivatives of HOTeF_5 and $\text{HN}(\text{SO}_2\text{CF}_3)_2$: A Solution Multi-NMR Study and X-ray Crystal Structures of $(\text{CH}_3)_3\text{SnCl}(\text{OTeF}_5)$ and $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$

Ashwani Vij,^a William W. Wilson,^a Vandana Vij,^a Robert C. Corley,^a Fook S. Tham,^b Michael Gerken,^c Ralf Haiges,^c Stefan Schneider,^c Thorsten Schroer^c and Ross I. Wagner,^c

^a Propulsion Sciences and Advanced Concepts Division, Air Force Research Laboratory (AFRL/PRS), Edwards Air Force Base, CA 93524, USA, ^b Department of Chemistry, University of California, Riverside, CA 92521, ^c Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA

The reaction of $(\text{CH}_3)_3\text{SnCl}$ with HOTeF_5 or ClOTeF_5 yields $(\text{CH}_3)_3\text{SnCl}(\text{OTeF}_5)$ which was characterized by multi-NMR and vibrational spectroscopy and by single crystal X-ray diffraction. The NMR spectroscopic study of $(\text{CH}_3)_3\text{SnOTeF}_5$ revealed the presence of tetraordinated tin in CH_2Cl_2 and as a neat liquid. In the donor solvents, acetone and CH_3CN , one solvent molecule coordinates on tin, while DMSO was found to cause Sn-OTeF_5 bond cleavage with formation of the $[(\text{CH}_3)_3\text{Sn}(\text{O}=\text{S}(\text{CH}_3)_2)_2][\text{OTeF}_5]$ salt. The salt $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ was characterized by X-ray crystallography.



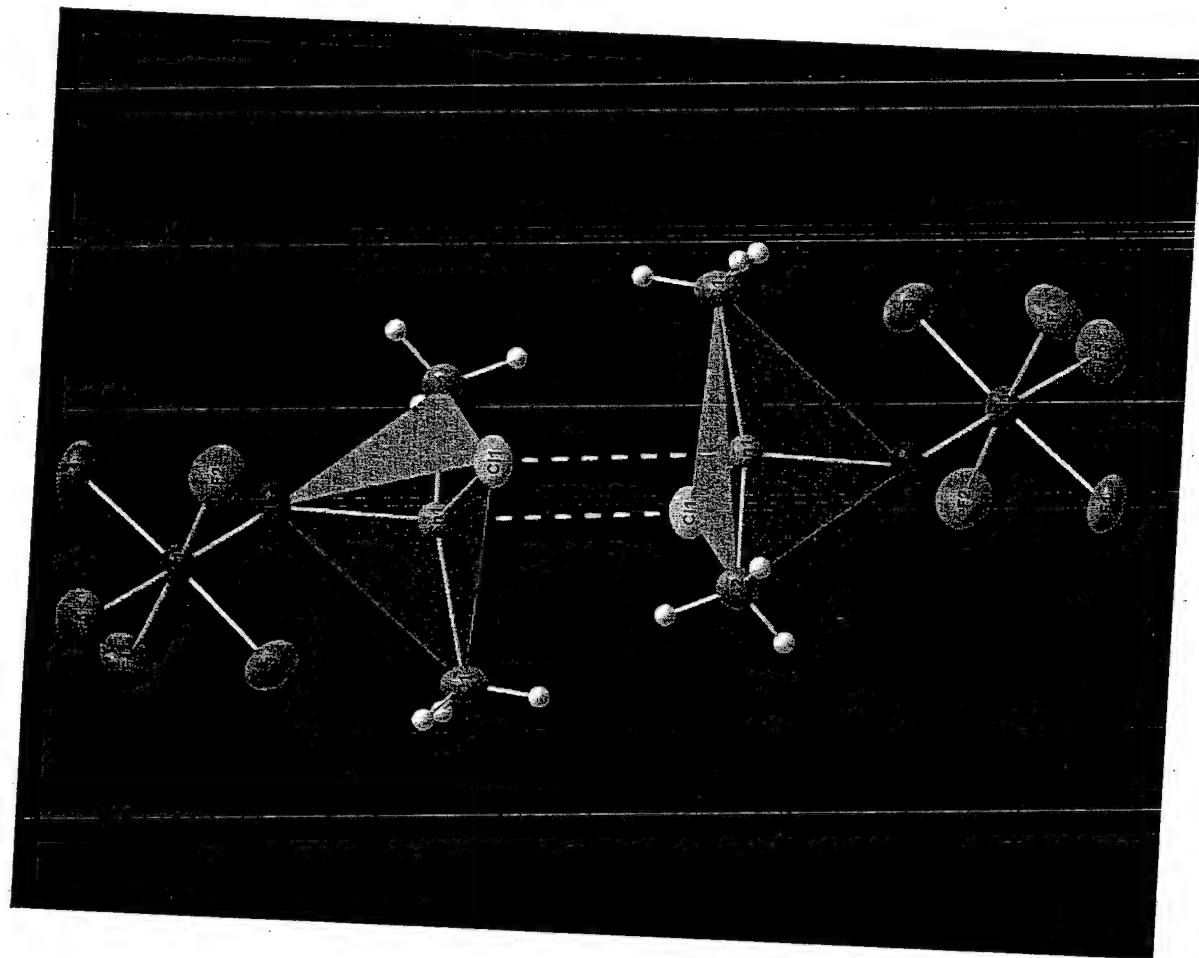


Fig. 1

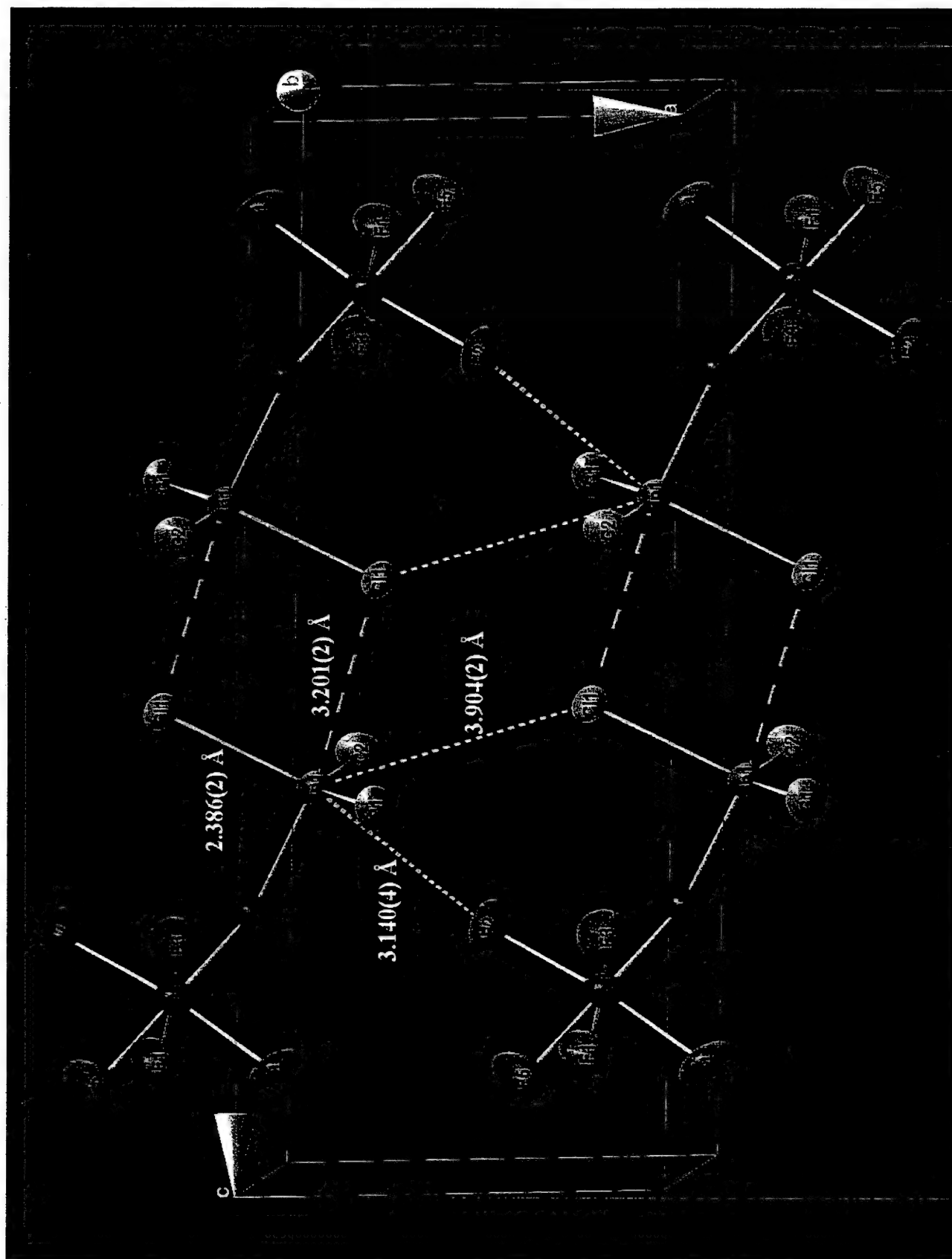


Fig. 2

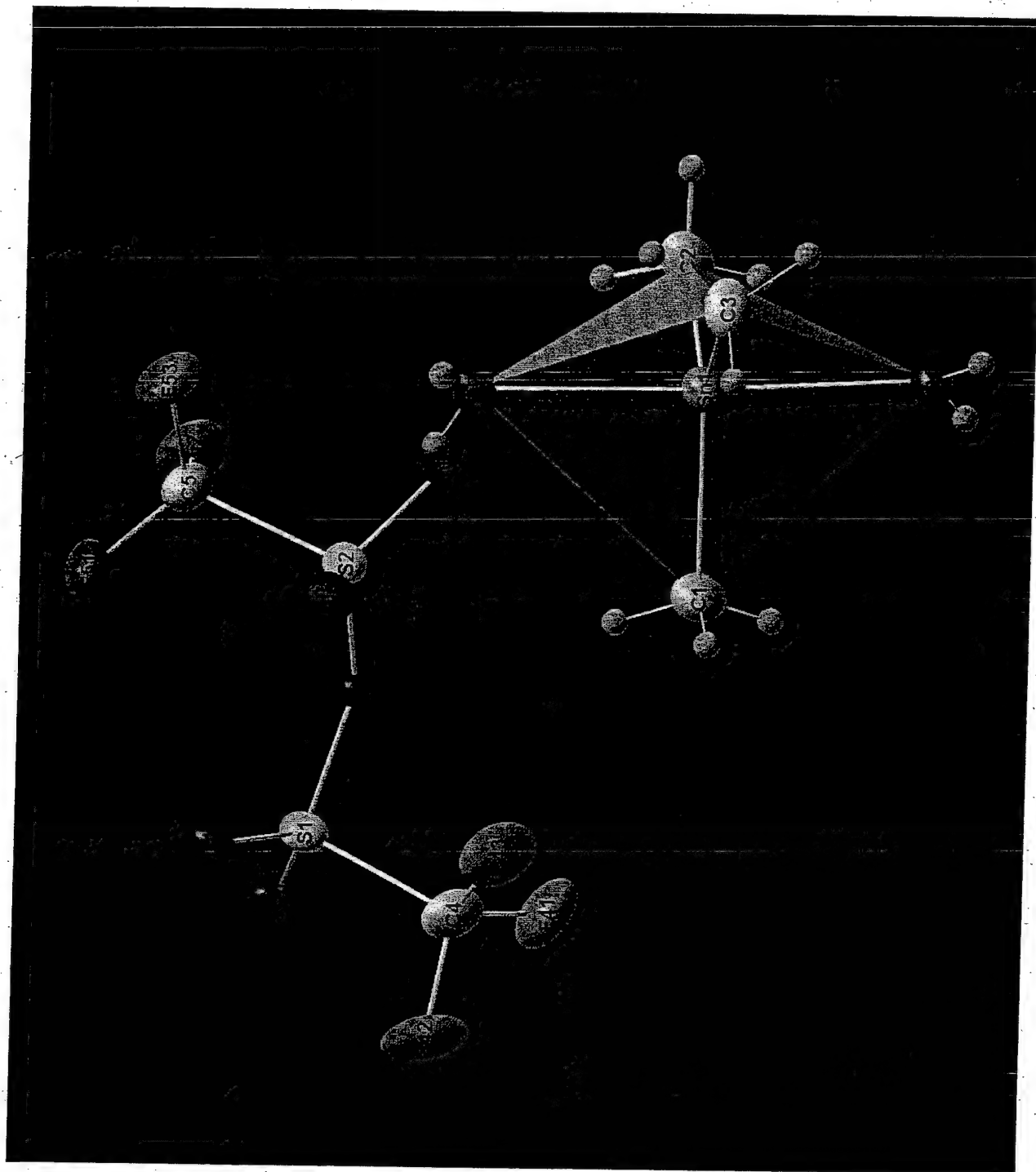


Fig. 3

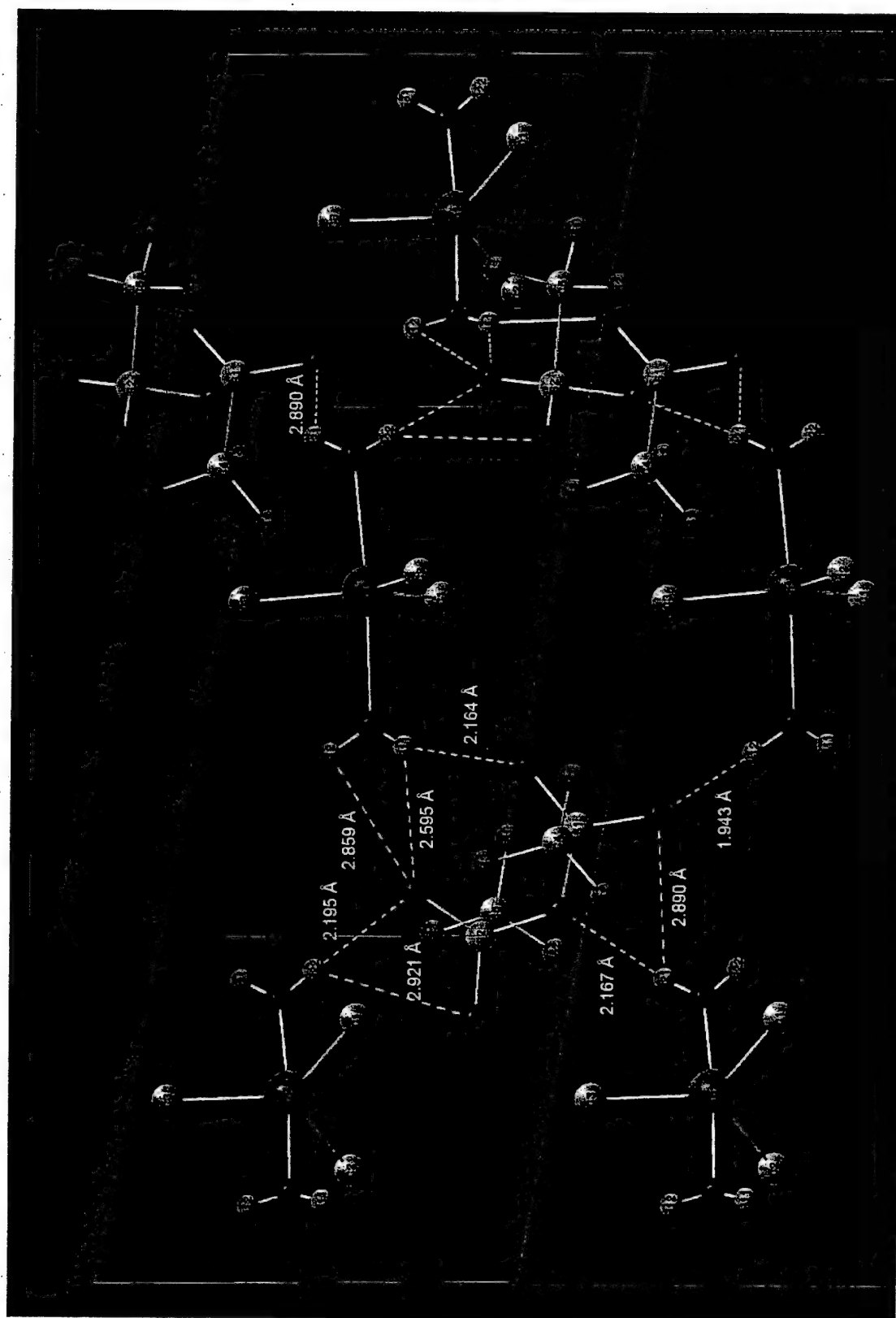


Fig. 4

Supplementary Material

Methyl Tin(IV) Derivatives of HOTeF_5 and $\text{HN}(\text{SO}_2\text{CF}_3)_2$: A Solution Multi-NMR Study and X-ray Crystal Structures of $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ and $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$

Ashwani Vij,^{*a} William W. Wilson,^a Vandana Vij,^a Robert C. Corley,^a Fook S. Tham,^b Michael Gerken,^c Ralf Haiges,^c Stefan Schneider,^c Thorsten Schroer^c and Ross I. Wagner,^c

^a *Propulsion Sciences and Advanced Concepts Division, Air Force Research Laboratory (AFRL/PRS), Edwards Air Force Base, CA 93524, USA,* ^b *Department of Chemistry, University of California, Riverside, CA 92521,* ^c *Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA*

Table 1. Crystal data and structure refinement for Me₂SnCl(OTeF₅)

Identification code	Me ₂ SnCl(OTeF ₅)	
Empirical formula	Me ₂ SnCl(OTeF ₅)	
Formula weight	422.81	
Temperature	218(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 5.8204(8) Å	∠ = 90°.
	b = 10.7820(14) Å	∠ = 91.958(2)°.
	c = 15.493(2) Å	∠ = 90°.
Volume	971.7(2) Å ³	
Z	4	
Density (calculated)	2.890 Mg/m ³	
Absorption coefficient	5.872 mm ⁻¹	
F(000)	760	
Crystal size	0.30 x 0.22 x 0.15 mm ³	
Theta range for data collection	2.30 to 29.30°.	
Index ranges	-7<=h<=8, -14<=k<=14, -16<=l<=21	
Reflections collected	6283	
Independent reflections	2360 [R(int) = 0.0277]	
Completeness to theta = 29.30°	89.3 %	
Absorption correction	SADABS	
Max. and min. transmission	0.4729 and 0.2718	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2360 / 0 / 103	
Goodness-of-fit on F ²	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0712	
R indices (all data)	R1 = 0.0333, wR2 = 0.0743	
Extinction coefficient	0.0042(3)	
Largest diff. peak and hole	0.864 and -0.672 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Sn(1)	11163(1)	4491(1)	1319(1)	27(1)
C(1)	12430(8)	2757(4)	955(3)	39(1)
C(2)	12389(7)	6282(4)	1585(3)	38(1)
Cl(1)	7508(2)	4728(1)	594(1)	40(1)
O(1)	9823(5)	3885(3)	2462(2)	38(1)
Te(1)	7968(1)	4479(1)	3274(1)	32(1)
F(1)	7791(5)	2965(3)	3804(2)	53(1)
F(2)	5315(4)	4095(4)	2639(2)	60(1)
F(3)	7841(5)	6060(3)	2823(2)	60(1)
F(4)	10350(6)	4924(4)	3999(2)	70(1)
F(5)	6072(6)	5041(3)	4094(2)	72(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$.

Sn(1)-O(1)	2.065(3)	Te(1)-F(5)	1.815(3)
Sn(1)-C(2)	2.094(4)	Te(1)-F(4)	1.819(3)
Sn(1)-C(1)	2.094(4)	Te(1)-F(1)	1.831(3)
Sn(1)-Cl(1)	2.3858(11)	Te(1)-F(3)	1.843(3)
O(1)-Te(1)	1.803(3)	Te(1)-F(2)	1.849(3)
O(1)-Sn(1)-C(2)	105.04(15)	F(5)-Te(1)-F(1)	86.50(14)
O(1)-Sn(1)-C(1)	95.44(14)	F(4)-Te(1)-F(1)	90.65(16)
C(2)-Sn(1)-C(1)	139.05(17)	O(1)-Te(1)-F(3)	94.68(13)
O(1)-Sn(1)-Cl(1)	94.64(9)	F(5)-Te(1)-F(3)	86.48(14)
C(2)-Sn(1)-Cl(1)	106.63(13)	F(4)-Te(1)-F(3)	90.54(17)
C(1)-Sn(1)-Cl(1)	106.58(13)	F(1)-Te(1)-F(3)	172.81(12)
Te(1)-O(1)-Sn(1)	137.59(17)	O(1)-Te(1)-F(2)	93.38(14)
O(1)-Te(1)-F(5)	178.67(15)	F(5)-Te(1)-F(2)	85.99(16)
O(1)-Te(1)-F(4)	93.57(15)	F(4)-Te(1)-F(2)	173.05(14)
F(5)-Te(1)-F(4)	87.06(16)	F(1)-Te(1)-F(2)	88.89(14)
O(1)-Te(1)-F(1)	92.33(12)	F(3)-Te(1)-F(2)	89.06(16)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Sn(1)	25(1)	29(1)	26(1)	1(1)	-2(1)	0(1)
C(1)	45(2)	33(2)	40(2)	0(2)	7(2)	5(2)
C(2)	36(2)	33(2)	45(2)	-8(2)	4(2)	-6(2)
Cl(1)	24(1)	61(1)	33(1)	9(1)	-5(1)	-3(1)
O(1)	40(2)	43(2)	31(1)	6(1)	7(1)	8(1)
Te(1)	31(1)	37(1)	30(1)	3(1)	3(1)	2(1)
F(1)	59(2)	52(2)	49(2)	22(1)	14(1)	6(1)
F(2)	31(1)	77(2)	70(2)	12(2)	-10(1)	-5(1)
F(3)	71(2)	34(1)	74(2)	11(1)	12(2)	8(1)
F(4)	67(2)	92(2)	49(2)	-14(2)	-20(2)	-9(2)
F(5)	80(2)	76(2)	64(2)	-3(2)	38(2)	23(2)

Table 5. Torsion angles [$^\circ$] for $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$.

C(2)-Sn(1)-O(1)-Te(1)	46.5(3)
C(1)-Sn(1)-O(1)-Te(1)	-169.3(3)
Cl(1)-Sn(1)-O(1)-Te(1)	-62.1(3)
Sn(1)-O(1)-Te(1)-F(5)	143(6)
Sn(1)-O(1)-Te(1)-F(4)	-98.3(3)
Sn(1)-O(1)-Te(1)-F(1)	170.9(3)
Sn(1)-O(1)-Te(1)-F(3)	-7.5(3)
Sn(1)-O(1)-Te(1)-F(2)	81.8(3)

Symmetry transformations used to generate equivalent atoms:

Table 6 - Contact Distances(Angstrom) for: Me₂SnCl(OTeF₅)

Sn1	.Cl1_a	3.9050(12)	F1	.H2C_f	2.6139
Sn1	.F2_a	3.141(3)	F1	.H2B_e	2.7936
Sn1	.Sn1_b	4.4008(7)	F2	.H1B_c	2.8020
Sn1	.Cl1_b	3.2013(12)	F3	.H2A	2.7659
Cl1	.Sn1_c	3.9050(12)	F5	.H1A_i	2.6796
Cl1	.Cl1_b	3.5373(15)	C1	.F4_f	3.316(6)
Cl1	.Sn1_b	3.2013(12)	C1	.Cl1_b	3.622(5)
Cl1	.Cl1_d	3.4470(15)	C2	.F2_a	3.307(6)
Cl1	.C1_b	3.622(5)	C2	.F3	3.330(5)
Cl1	.C2_b	3.549(5)	C2	.Cl1_b	3.549(5)
Cl1	.H2C_c	3.0201	H1A	.F5_e	2.6796
Cl1	.H1C_b	3.1027	H1B	.F2_a	2.8020
F2	.Sn1_c	3.141(3)	H1C	.Cl1_b	3.1027
F2	.C2_c	3.307(6)	H1C	.F1_k	2.4907
F3	.C2	3.330(5)	H2A	.F3	2.7659
F4	.C1_h	3.316(6)	H2B	.F1_i	2.7936
F5	.F5_j	3.112(5)	H2C	.Cl1_a	3.0201
F1	.H1C_g	2.4907	H2C	.F1_h	2.6139

Table 7 - Hydrogen Bonds (Angstrom, Deg) for: Me₂SnCl(OTeF₅)

Cl -- H1C .. F1 0.969(5) 2.491(3) 3.436(5) 165.0(3) 4_554

Translation of Symmetry Code to Equiv.Pos

a=[1655.00] = 1+x,y,z

b=[3765.00] = 2-x,1-y,-z

c=[1455.00] = -1+x,y,z

d=[3665.00] = 1-x,1-y,-z

e=[2645.00] = 3/2-x,-1/2+y,1/2-z

f=[2745.00] = 5/2-x,-1/2+y,1/2-z

g=[4455.00] = -1/2+x,1/2-y,1/2+z

h=[2755.00] = 5/2-x,1/2+y,1/2-z

i=[2655.00] = 3/2-x,1/2+y,1/2-z

j=[3666.00] = 1-x,1-y,1-z

k=[4554.00] = 1/2+x,1/2-y,-1/2+z

Table 8. Crystal data and structure refinement for $[\text{Me}_3\text{Sn}(\text{H}_2\text{O})_2]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$

Identification code	$[\text{Me}_3\text{Sn}(\text{H}_2\text{O})]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$
Empirical formula	$\text{C}_5 \text{H}_{13} \text{F}_6 \text{N} \text{O}_6 \text{S}_2 \text{Sn}$
Formula weight	479.97
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	$a = 7.30720(10) \text{ Å}$ $\alpha = 90^\circ$ $b = 13.4649(2) \text{ Å}$ $\beta = 98.7050(10)^\circ$ $c = 16.821 \text{ Å}$ $\gamma = 90^\circ$
Volume	$1636.00(3) \text{ Å}^3$
Z	4
Density (calculated)	1.949 Mg/m^3
Absorption coefficient	1.898 mm^{-1}
F(000)	936
Crystal size	$0.30 \times 0.20 \times 0.12 \text{ mm}^3$
Theta range for data collection	1.95 to 28.27°
Index ranges	$-9 \leq h \leq 9$, $-17 \leq k \leq 17$, $-13 \leq l \leq 22$
Reflections collected	20558
Independent reflections	3908 [$R(\text{int}) = 0.0327$]
Absorption correction	SADABS
Max. and min. transmission	0.965354 and 0.853923
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3908 / 0 / 207
Goodness-of-fit on F^2	1.233
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0367$, $wR_2 = 0.0736$
R indices (all data)	$R_1 = 0.0410$, $wR_2 = 0.0759$
Extinction coefficient	0.0131(4)
Largest diff. peak and hole	0.468 and -0.426 e. Å^{-3}

Table 9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Me}_3\text{Sn}(\text{H}_2\text{O})_2]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Sn(1)	4149(1)	3482(1)	3474(1)	34(1)
S(1)	9913(1)	2698(1)	715(1)	34(1)
S(2)	7793(1)	4113(1)	1397(1)	33(1)
F(41)	11105(5)	1580(2)	1948(2)	92(1)
F(42)	9976(5)	794(2)	892(3)	95(1)
F(43)	8150(5)	1537(2)	1581(2)	91(1)
F(51)	7822(4)	4885(2)	-30(2)	71(1)
F(52)	9275(5)	5742(2)	944(2)	83(1)
F(53)	6284(4)	5708(2)	735(2)	84(1)
O(1)	4717(4)	2953(3)	4793(2)	46(1)
O(2)	3362(4)	4046(3)	2154(2)	47(1)
O(3)	11785(3)	2708(2)	566(2)	50(1)
O(4)	8467(3)	2594(2)	47(2)	49(1)
O(5)	6150(3)	3569(2)	1095(2)	44(1)
O(6)	7930(4)	4542(2)	2176(2)	52(1)
N(1)	9685(4)	3569(2)	1316(2)	33(1)
C(1)	5633(7)	2277(4)	3077(3)	58(1)
C(2)	5613(6)	4801(3)	3803(3)	55(1)
C(3)	1289(5)	3384(3)	3560(2)	49(1)
C(4)	9778(7)	1586(3)	1324(3)	59(1)
C(5)	7801(6)	5181(3)	711(3)	53(1)

Table 10. Bond lengths [\AA] and angles [$^\circ$] for $[\text{Me}_3\text{Sn}(\text{H}_2\text{O})_2]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$

Sn(1)-C(2)	2.104(4)	F(51)-C(5)	1.311(5)
Sn(1)-C(1)	2.115(4)	F(52)-C(5)	1.325(5)
Sn(1)-C(3)	2.120(4)	F(53)-C(5)	1.322(5)
Sn(1)-O(1)	2.306(3)	O(1)-H(12)	0.87(6)
Sn(1)-O(2)	2.335(3)	O(1)-H(11)	0.69(5)
S(1)-O(3)	1.427(2)	O(2)-H(22)	0.78(7)
S(1)-O(4)	1.428(3)	O(2)-H(21)	0.76(6)
S(1)-N(1)	1.573(3)	C(1)-H(1A)	0.97
S(1)-C(4)	1.825(5)	C(1)-H(1B)	0.97
S(2)-O(6)	1.421(3)	C(1)-H(1C)	0.97
S(2)-O(5)	1.433(3)	C(2)-H(2A)	0.97
S(2)-N(1)	1.589(3)	C(2)-H(2B)	0.97
S(2)-C(5)	1.844(4)	C(2)-H(2C)	0.97
F(41)-C(4)	1.316(6)	C(3)-H(3A)	0.97
F(42)-C(4)	1.312(5)	C(3)-H(3B)	0.97
F(43)-C(4)	1.327(6)	C(3)-H(3C)	0.97
C(2)-Sn(1)-C(1)	117.8(2)	O(6)-S(2)-O(5)	118.2(2)
C(2)-Sn(1)-C(3)	120.1(2)	O(6)-S(2)-N(1)	109.0(2)
C(1)-Sn(1)-C(3)	122.1(2)	O(5)-S(2)-N(1)	115.3(2)
C(2)-Sn(1)-O(1)	89.83(15)	O(6)-S(2)-C(5)	104.7(2)
C(1)-Sn(1)-O(1)	92.3(2)	O(5)-S(2)-C(5)	105.0(2)
C(3)-Sn(1)-O(1)	87.19(13)	N(1)-S(2)-C(5)	102.7(2)
C(2)-Sn(1)-O(2)	91.04(15)	Sn(1)-O(1)-H(12)	121.1(32)
C(1)-Sn(1)-O(2)	90.8(2)	Sn(1)-O(1)-H(11)	122.2(43)
C(3)-Sn(1)-O(2)	88.95(13)	H(12)-O(1)-H(11)	110.1(54)
O(1)-Sn(1)-O(2)	175.94(11)	Sn(1)-O(2)-H(22)	114.3(47)
O(3)-S(1)-O(4)	118.5(2)	Sn(1)-O(2)-H(21)	122.2(41)
O(3)-S(1)-N(1)	107.6(2)	H(22)-O(2)-H(21)	111.5(58)
O(4)-S(1)-N(1)	116.1(2)	S(1)-N(1)-S(2)	125.3(2)
O(3)-S(1)-C(4)	104.0(2)	Sn(1)-C(1)-H(1A)	109.47(14)
O(4)-S(1)-C(4)	105.4(2)	Sn(1)-C(1)-H(1B)	109.47(13)
N(1)-S(1)-C(4)	103.4(2)	H(1A)-C(1)-H(1B)	109.5

Sn(1)-C(1)-H(1C)	109.47(13)
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
Sn(1)-C(2)-H(2A)	109.47(13)
Sn(1)-C(2)-H(2B)	109.47(12)
H(2A)-C(2)-H(2B)	109.5
Sn(1)-C(2)-H(2C)	109.47(13)
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
Sn(1)-C(3)-H(3A)	109.47(13)
Sn(1)-C(3)-H(3B)	109.47(11)
H(3A)-C(3)-H(3B)	109.5
Sn(1)-C(3)-H(3C)	109.47(11)
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
F(42)-C(4)-F(41)	107.9(4)
F(42)-C(4)-F(43)	108.6(4)
F(41)-C(4)-F(43)	109.2(5)
F(42)-C(4)-S(1)	109.6(4)
F(41)-C(4)-S(1)	110.9(3)
F(43)-C(4)-S(1)	110.5(3)
F(51)-C(5)-F(53)	108.8(4)
F(51)-C(5)-F(52)	109.2(4)
F(53)-C(5)-F(52)	109.5(4)
F(51)-C(5)-S(2)	111.1(3)
F(53)-C(5)-S(2)	108.5(3)
F(52)-C(5)-S(2)	109.8(3)

Table 11. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_3\text{Sn}(\text{H}_2\text{O})_2^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Sn(1)	26(1)	43(1)	34(1)	-1(1)	7(1)	-2(1)
S(1)	24(1)	40(1)	40(1)	-7(1)	8(1)	1(1)
S(2)	27(1)	39(1)	34(1)	0(1)	9(1)	4(1)
F(41)	108(3)	70(2)	91(2)	31(2)	-4(2)	21(2)
F(42)	107(3)	39(2)	145(3)	-15(2)	36(2)	9(2)
F(43)	90(2)	60(2)	138(3)	26(2)	66(2)	-3(2)
F(51)	87(2)	79(2)	52(2)	25(1)	25(1)	26(2)
F(52)	88(2)	49(2)	118(3)	9(2)	34(2)	-16(2)
F(53)	84(2)	74(2)	101(2)	29(2)	35(2)	50(2)
O(1)	28(1)	68(2)	42(2)	14(1)	6(1)	3(1)
O(2)	29(1)	78(2)	35(1)	6(1)	5(1)	-6(1)
O(3)	28(1)	65(2)	59(2)	-11(1)	15(1)	2(1)
O(4)	32(1)	71(2)	45(2)	-19(1)	5(1)	-1(1)
O(5)	26(1)	55(2)	52(2)	-5(1)	12(1)	-2(1)
O(6)	53(2)	64(2)	41(1)	-14(1)	12(1)	12(1)
N(1)	24(1)	38(2)	37(1)	-5(1)	2(1)	3(1)
C(1)	63(3)	58(3)	57(3)	-1(2)	24(2)	13(2)
C(2)	61(3)	57(3)	48(2)	-8(2)	12(2)	-20(2)
C(3)	29(2)	72(3)	46(2)	13(2)	8(2)	0(2)
C(4)	61(3)	40(2)	78(3)	6(2)	21(2)	4(2)
C(5)	54(2)	47(2)	60(3)	11(2)	20(2)	15(2)

Table 12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Me}_3\text{Sn}(\text{H}_2\text{O})_2]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$

	x	y	z	U(eq)
H(12)	3828(75)	2721(39)	5032(30)	68(16)
H(11)	5549(74)	2747(39)	4958(30)	59(16)
H(22)	4068(91)	3903(50)	1870(38)	94(22)
H(21)	2369(79)	4031(41)	1934(32)	68(17)
H(1A)	4803(7)	1719(4)	2945(3)	87
H(1B)	6623(7)	2085(4)	3500(3)	87
H(1C)	6154(7)	2474(4)	2604(3)	87
H(2A)	4777(6)	5291(3)	3973(3)	82
H(2B)	6133(6)	5055(3)	3346(3)	82
H(2C)	6602(6)	4666(3)	4243(3)	82
H(3A)	833(5)	2730(3)	3386(2)	73
H(3B)	616(5)	3885(3)	3220(2)	73
H(3C)	1111(5)	3490(3)	4113(2)	73

Table 13. Torsion angles [°] for $[\text{Me}_3\text{Sn}(\text{H}_2\text{O})_2]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$

O(3)-S(1)-N(1)-S(2)	155.0(2)
O(4)-S(1)-N(1)-S(2)	19.5(3)
C(4)-S(1)-N(1)-S(2)	-95.4(3)
O(6)-S(2)-N(1)-S(1)	156.3(2)
O(5)-S(2)-N(1)-S(1)	20.6(3)
C(5)-S(2)-N(1)-S(1)	-93.0(3)
O(3)-S(1)-C(4)-F(42)	-66.8(4)
O(4)-S(1)-C(4)-F(42)	58.5(4)
N(1)-S(1)-C(4)-F(42)	-179.2(3)
O(3)-S(1)-C(4)-F(41)	52.2(4)
O(4)-S(1)-C(4)-F(41)	177.5(3)
N(1)-S(1)-C(4)-F(41)	-60.1(4)
O(3)-S(1)-C(4)-F(43)	173.5(4)
O(4)-S(1)-C(4)-F(43)	-61.2(4)
N(1)-S(1)-C(4)-F(43)	61.1(4)
O(6)-S(2)-C(5)-F(51)	175.2(3)
O(5)-S(2)-C(5)-F(51)	-59.6(3)
N(1)-S(2)-C(5)-F(51)	61.3(3)
O(6)-S(2)-C(5)-F(53)	-65.3(4)
O(5)-S(2)-C(5)-F(53)	60.0(4)
N(1)-S(2)-C(5)-F(53)	-179.2(3)
O(6)-S(2)-C(5)-F(52)	54.3(3)
O(5)-S(2)-C(5)-F(52)	179.5(3)
N(1)-S(2)-C(5)-F(52)	-59.6(3)

Symmetry transformations used to generate equivalent atoms:

Table 14 - Contact Distances(Angstrom) for $[\text{Me}_3\text{Sn}(\text{H}_2\text{O})_2]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$

S1	.F51	3.464(3)	O2	.N1_k	2.911(4)
S1	.H21_a	3.08(5)	O2	.O5	2.972(4)
S2	.H22	2.96(7)	O3	.F42	2.985(4)
F41	.O3	2.882(4)	O3	.F41	2.882(4)
F41	.N1	3.008(4)	O3	.O1_f	2.814(4)
F41	.O6_b	3.144(4)	O4	.F43	2.986(4)
F42	.O3	2.985(4)	O4	.F51	3.120(4)
F42	.O4	2.939(4)	O4	.O1_g	2.807(4)
F43	.O4	2.986(4)	O4	.O5	2.933(4)
F43	.O5	3.151(4)	O4	.F42	2.939(4)
F43	.N1	3.016(4)	O5	.F51	2.986(4)
F51	.O4	3.120(4)	O5	.F43	3.151(4)
F51	.O5	2.986(4)	O5	.O4	2.933(4)
F51	.S1	3.464(3)	O5	.O2	2.972(4)
F51	.F52_d	2.926(5)	O5	.O1_g	3.066(5)
F51	.N1	3.031(4)	O5	.F53	2.948(4)
F52	.N1	2.998(4)	O6	.F52	2.913(4)
F52	.O6	2.913(4)	O6	.F41_h	3.144(4)
F52	.F51_d	2.926(5)	O6	.F53	2.984(4)
F53	.O5	2.948(4)	O3	.H21_a	2.88(5)
F53	.O6	2.984(4)	O3	.H12_f	1.95(6)
F53	.C1_e	3.357(6)	O3	.H3C_f	2.908(5)
F43	.H1C	2.728(6)	O4	.H11_g	2.16(5)
F43	.H2A_c	2.767(5)	O4	.H1B_g	2.777(6)
F53	.H1A_e	2.819(6)	O5	.H11_g	2.60(5)
O1	.O4_j	2.807(4)	O5	.H12_g	2.86(5)
O1	.O5_j	3.066(5)	O5	.H22	2.19(7)
O1	.O3_i	2.814(4)	O6	.H3B_a	2.584(5)
O6	.H2B	2.619(6)	H3B	.O6_k	2.584(5)
N1	.O2_a	2.911(4)	H3C	.H12	2.54(6)
N1	.F43	3.016(4)	H3C	.O3_i	2.908(5)
N1	.F41	3.008(4)	H11	.O4_j	2.16(5)
N1	.F51	3.031(4)	H11	.O5_j	2.60(5)

N1	.F52	2.998(4)	H12	.H3C	2.54(6)
N1	.H21_a	2.17(6)	H12	.O3_i	1.95(6)
C1	.F53_l	3.357(6)	H12	.O5_j	2.86(5)
H1A	.F53_l	2.819(6)	H21	.S1_k	3.08(5)
H1B	.O4_j	2.777(6)	H21	.O3_k	2.88(5)
H1C	.F43	2.728(6)	H21	.N1_k	2.17(6)
H2A	.F43_m	2.767(5)	H22	.S2	2.96(7)
H2B	.O6	2.619(6)	H22	.O5	2.19(7)

Table 15 - Hydrogen Bonds (Angstrom, Deg) for $[\text{Me}_3\text{Sn}(\text{H}_2\text{O})_2]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$

O1	-- H11 .. O4	0.69(5)	2.16(5)	2.807(4)	156(6)	4_555
O1	-- H11 .. O5	0.69(5)	2.60(5)	3.066(5)	128(5)	4_555
O1	-- H12 .. O3	0.87(6)	1.95(6)	2.814(4)	176(5)	4_455
O2	-- H21 .. N1	0.76(6)	2.17(6)	2.911(4)	165(5)	1_455
O2	-- H22 .. O5	0.78(7)	2.19(7)	2.972(4)	177(7)	.
C3	-- H3B .. O6	0.969(5)	2.584(5)	3.485(5)	154.8(4)	1_455

Translation of Symmetry Code to Equiv.Pos.

$a = [1655.00] = 1+x, y, z$
 $b = [2745.00] = 2-x, -1/2+y, 1/2-z$
 $c = [2645.00] = 1-x, -1/2+y, 1/2-z$
 $d = [3765.00] = 2-x, 1-y, -z$
 $e = [2655.00] = 1-x, 1/2+y, 1/2-z$
 $f = [4654.00] = 1+x, 1/2-y, -1/2+z$
 $g = [4554.00] = x, 1/2-y, -1/2+z$
 $h = [2755.00] = 2-x, 1/2+y, 1/2-z$
 $i = [4455.00] = -1+x, 1/2-y, 1/2+z$
 $j = [4555.00] = x, 1/2-y, 1/2+z$
 $k = [1455.00] = -1+x, y, z$